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Supporting Information for

Theoretical Unimolecular Kinetics for $CH_4 + M \rightleftarrows CH_3 + H + M$ in Eight Baths, M = He, Ne, Ar, Kr, H_2, CO, N_2, and CH_4

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Table S-1. Fitted intermolecular potential energy surface parameters

Lennard-Jones parameters (eq 23)

M	Fit	Pair	D, cm^{-1}	R', Å
He	A	He–H	18.1	2.91
		He–C	80.0	2.66
	B	He–H	6.51	2.86
		He–C	15.9	3.16

exp/6 parameters (eq 24)

M	Fit	Pair	$\log_{10}(A/\text{cm}^{-1})$	B, Å	C, Å	S, Å
He	–	He–H	7.550	0.2522	4.510	
		He–C	6.714	0.2884	6.167	
Ne	–	Ne–H	6.391	0.2621	5.749	
		Ne–C	7.500	0.2391	4.802	
Ar[a]	–	Ar–H	6.602	0.2954	2.684	
		Ar–C	7.529	0.2772	2.663	
Kr[a]	–	Kr–H	6.682	0.3088	2.922	
		Kr–C	7.597	0.2841	2.540	
H_2	RP	H–H	4.912	0.3865	6.270	2.500
		H–C	5.140	0.4285	3.250	2.941
	R	H–H	5.239	0.3176	5.539	2.625
		H–C	6.916	0.2244	5.475	2.460
	P	H–H	5.681	0.2772	5.453	2.553
		H–C	6.250	0.2896	1.516	3.000
N_2	RP	N–H	6.528	0.2759	6.459	0.9430
		N–C	7.145	0.2861	0.02881	6.057
	R	N–H	6.351	0.2735	0.01758	8.710
		N–C	6.750	0.3008	8.438	2.849
	P	N–H	6.500	0.2600	4.496	3.099
		N–C	7.438	0.2652	8.188	3.050
CO	RP	C–H	7.127	0.2261	6.562	3.285
		C–C	7.500	0.2763	1.681	7.134
		O–H	5.000	0.3990	2.000	2.458
		O–C	6.000	0.3399	8.750	3.001
	R O-in	C–H	6.680	0.2922	0.7389	1.451
		C–C	7.188	0.2389	8.748	2.501
		O–H	5.000	0.4131	0.9066	8.748
		O–C	6.937	0.3032	8.985	2.293

[a]From Alexander; W. A.; Troya, D. *J. Phys. Chem.* **2006**, *110*, 10834.

Figure S-1

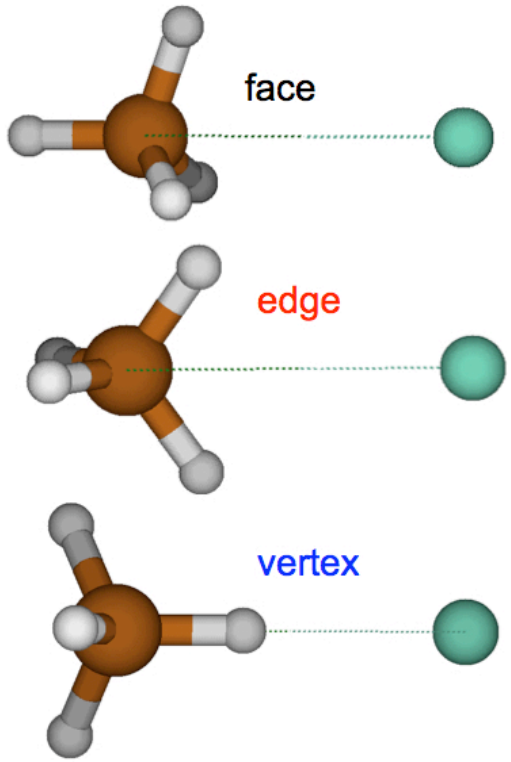

Fig. S-1. Representations of the three approaches considered for the atomic baths.

Figure S-2

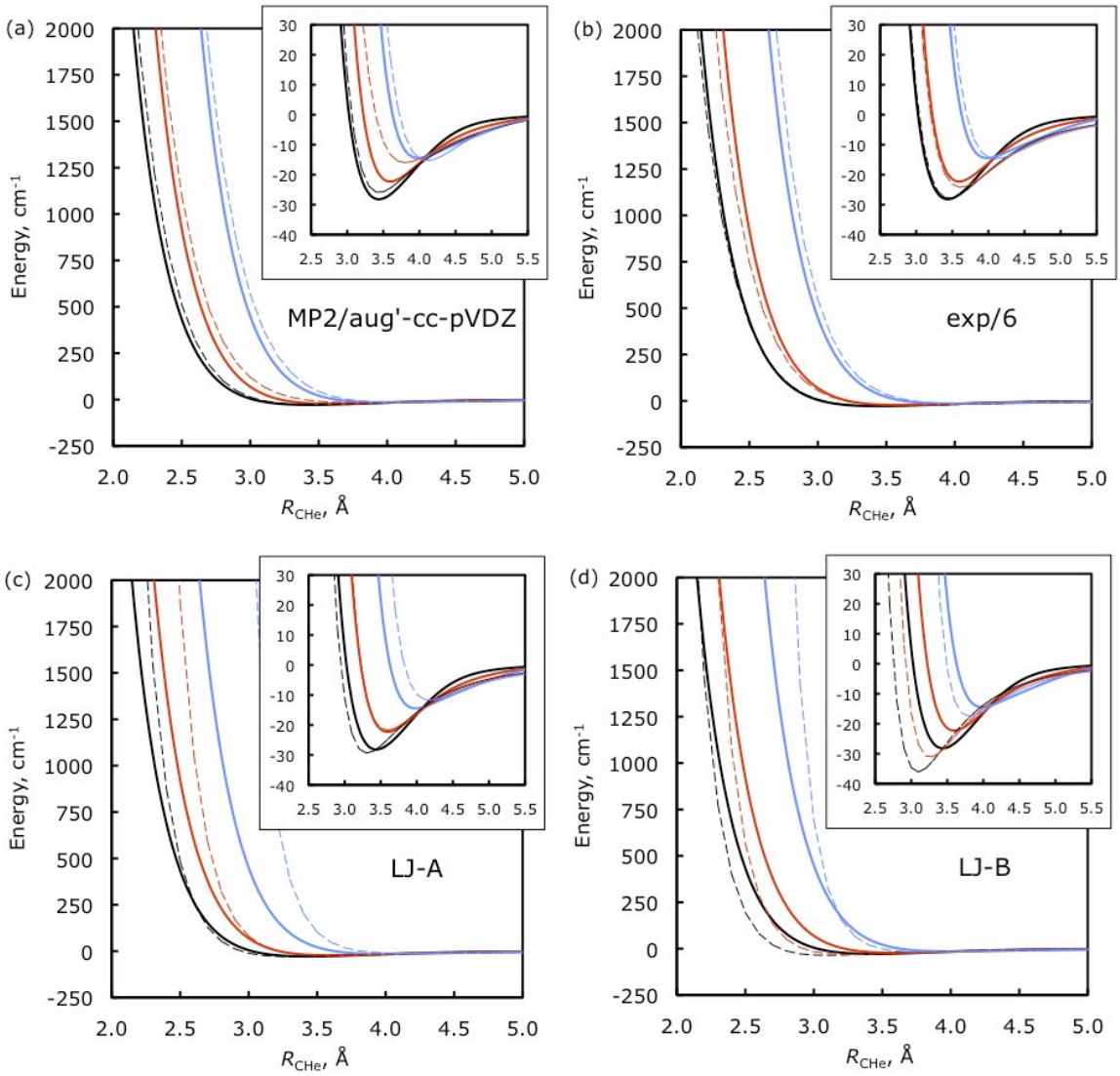

Fig. S-2 (Fig. 1 in the article) CH_4 + He interaction potential for face (black), edge (red), and vertex (blue) approaches. The solid lines in all four panels are QCISD(T)/CBS energies, and the dashed lines are (a) MP2/aug'-cc-pVDZ, (b) exp/6, (c) LJ-A, and (d) LJ-B energies. The insets highlight the van der Waals wells.

Figure S-3

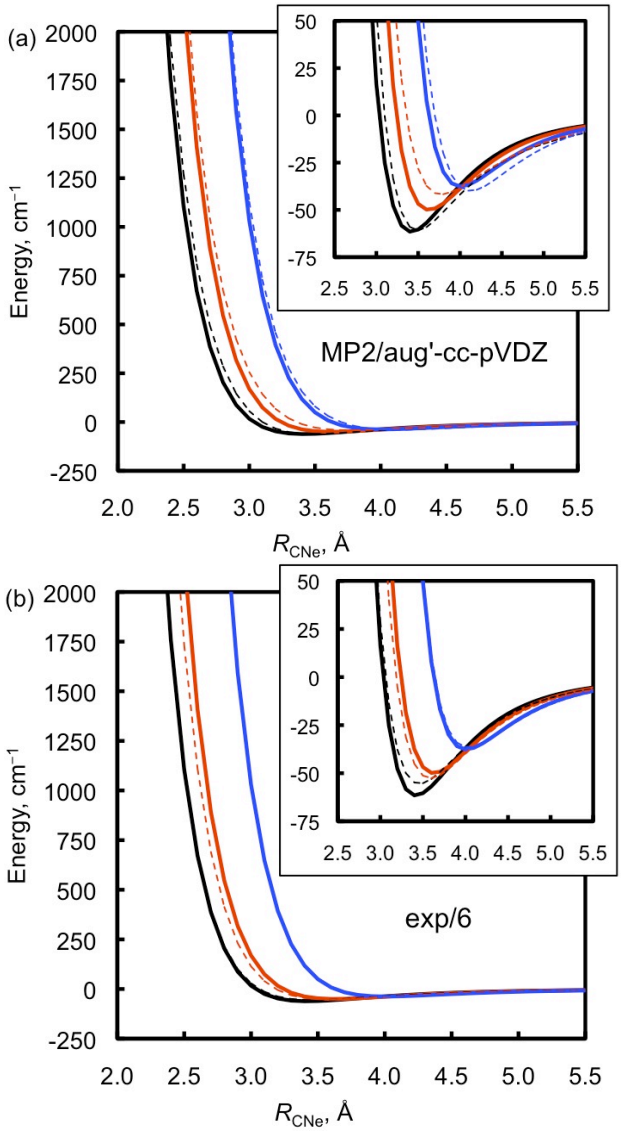

Fig. S-3 Comparison of the QCISD(T)/CBS CH_4 + Ne interaction potential along three approaches (solid) with those for the (a) MP2/aug'-cc-pVDZ and (b) exp/6 methods (dashed). The color code for the approaches is the same as in Fig. S-2.

Figure S-4

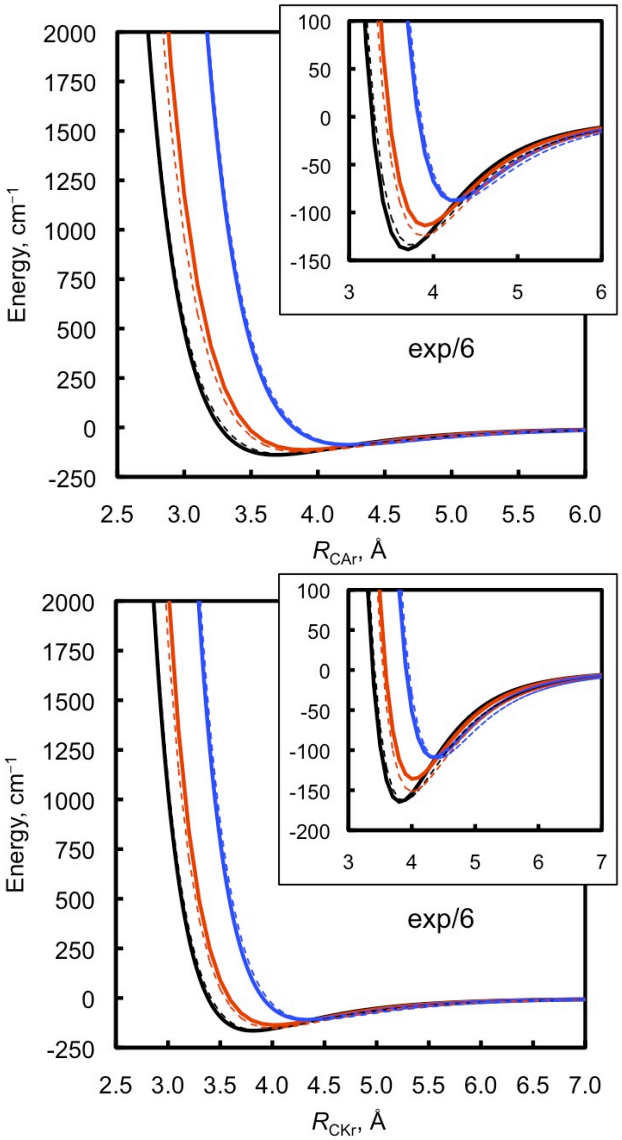

Fig. S-4 Comparison of the QCISD(T)/CBS CH_4 + M interaction potential (solid) along three approaches with those for the exp/6 method (dashed) for (a) Ar and (b) Kr. The color code for the approaches is the same as in Fig. S-2.

Figure S-5

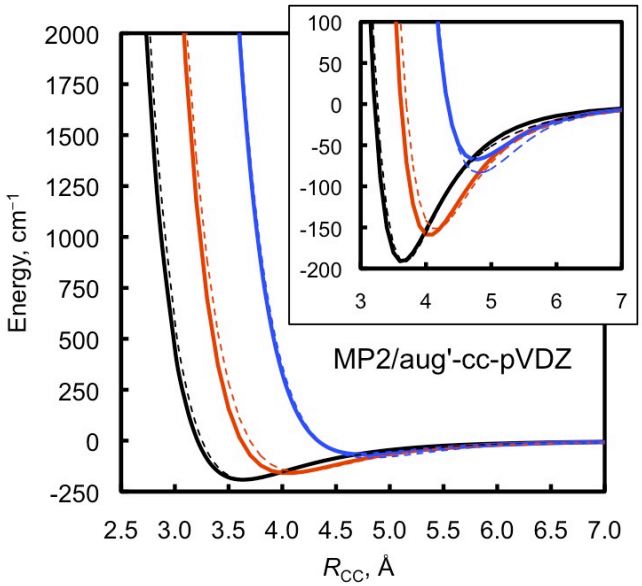

Fig. S-5 Comparison of the QCISD(T)/CBS CH_4 + CH_4 interaction potential (solid) along three approaches (black: face-face, red: face-vertex, blue: vertex-vertex) with those for the MP2/aug'-cc-pVDZ method (dashed).

Figure S-6

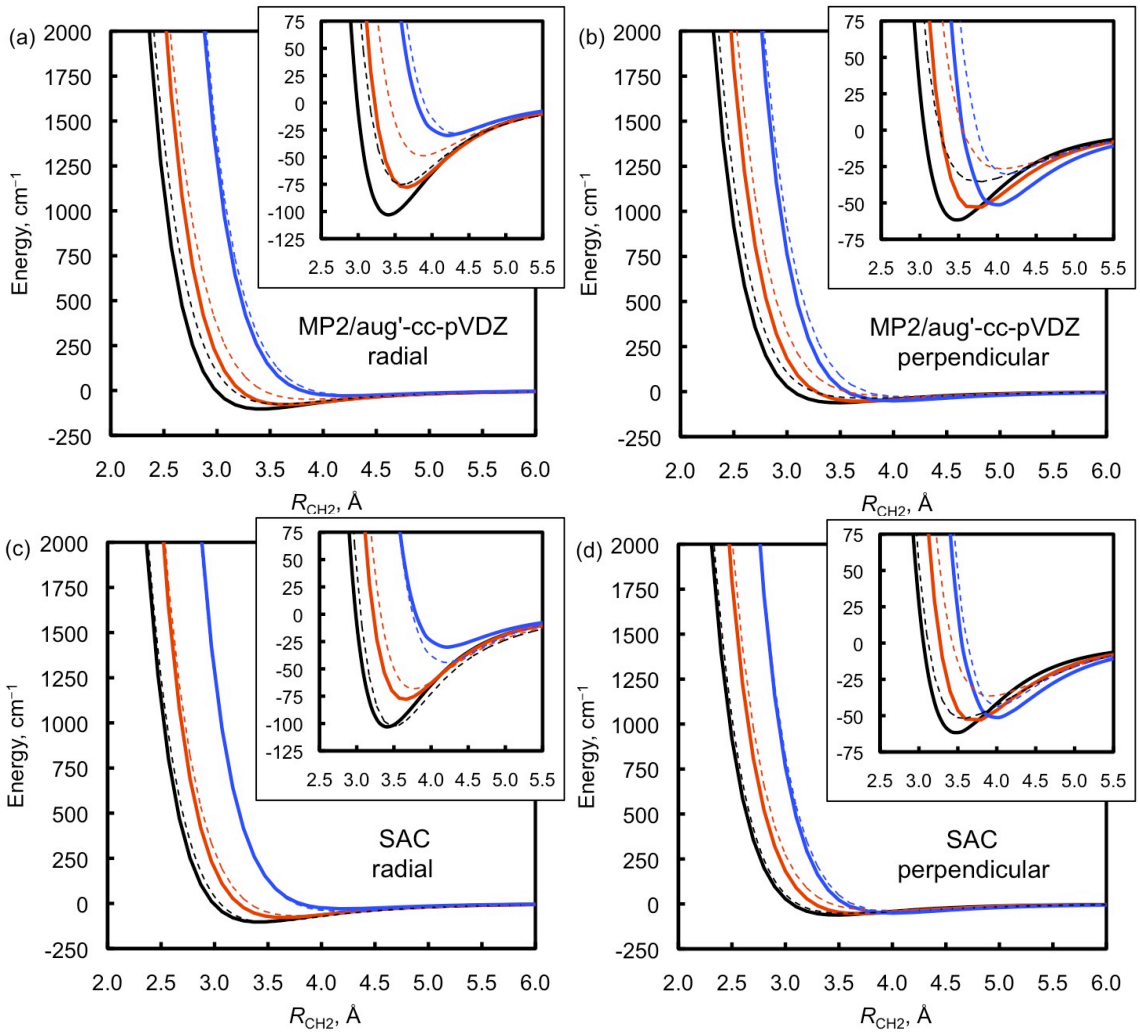

Fig. S-6 Comparison of the QCISD(T)/CBS $CH_4 + H_2$ interaction potential (solid) along six approaches with those for the (a,b) MP2/aug'-cc-pVDZ and (c,d) SAC/aug'-cc-pVDZ methods (dashed). The color code for the approaches is the same as in Fig. S-2. H_2 is aligned in the direction of the approach (radially) in (a,c) and perpendicular to the direction of approach in (b,d).

Figure S-7

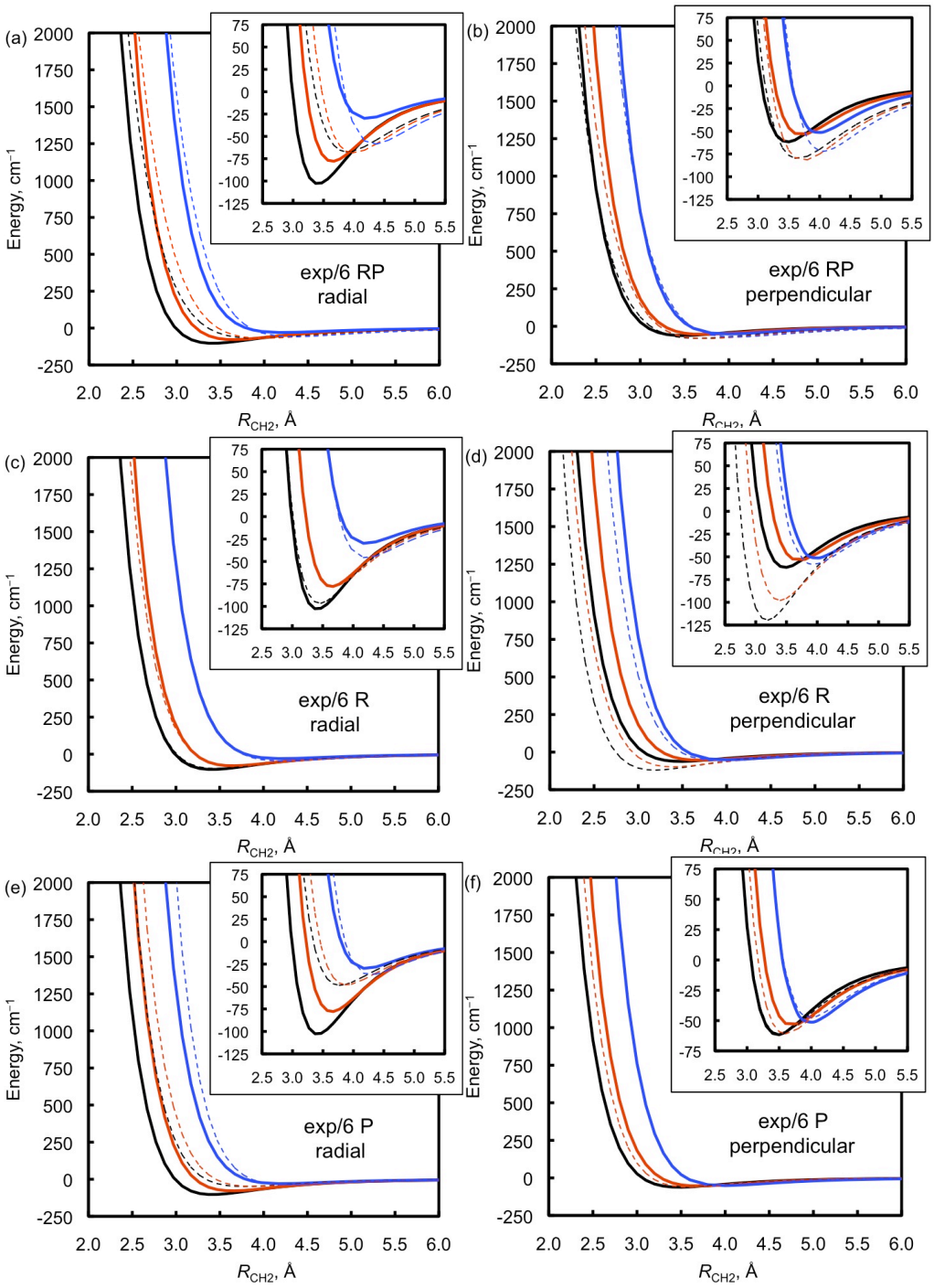

Fig. S-7 (Fig. 2 in the article) Comparison of the QCISD(T)/CBS $CH_4 + H_2$ interaction potential (solid) along six approaches with the exp/6 method for the (a,b) compromise (RP), (c,d) radial-only (R), and (e,f) perpendicular-only (P) fits (dashed). The color code for the approaches is the same as in Fig. S-2. H_2 is aligned in the direction of the approach (radially) in (a,c,e) and perpendicularly in (b,d,f).

Figure S-8

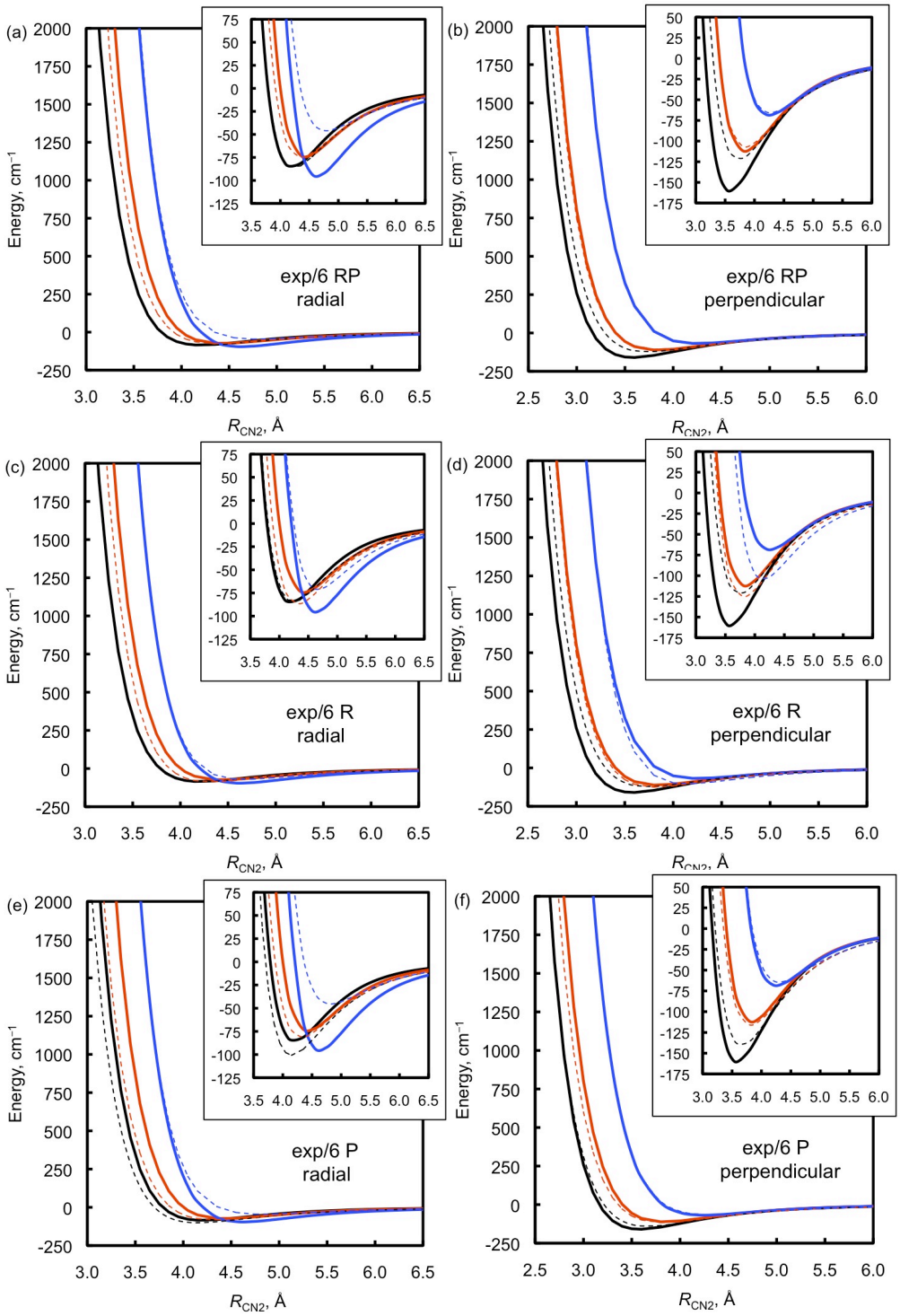

Fig. S-8 Comparison of the QCISD(T)/CBS $CH_4 + N_2$ interaction potential (solid) along six approaches with the exp/6 method for the (a,b) compromise (RP), (c,d) radial-only (R), and (e,f) perpendicular-only (P) fits (dashed). The color code for the approaches is the same as in Fig. S-2. N_2 is aligned in the direction of the approach (radially) in (a,c,e) and perpendicularly in (b,d,f).

Figure S-9

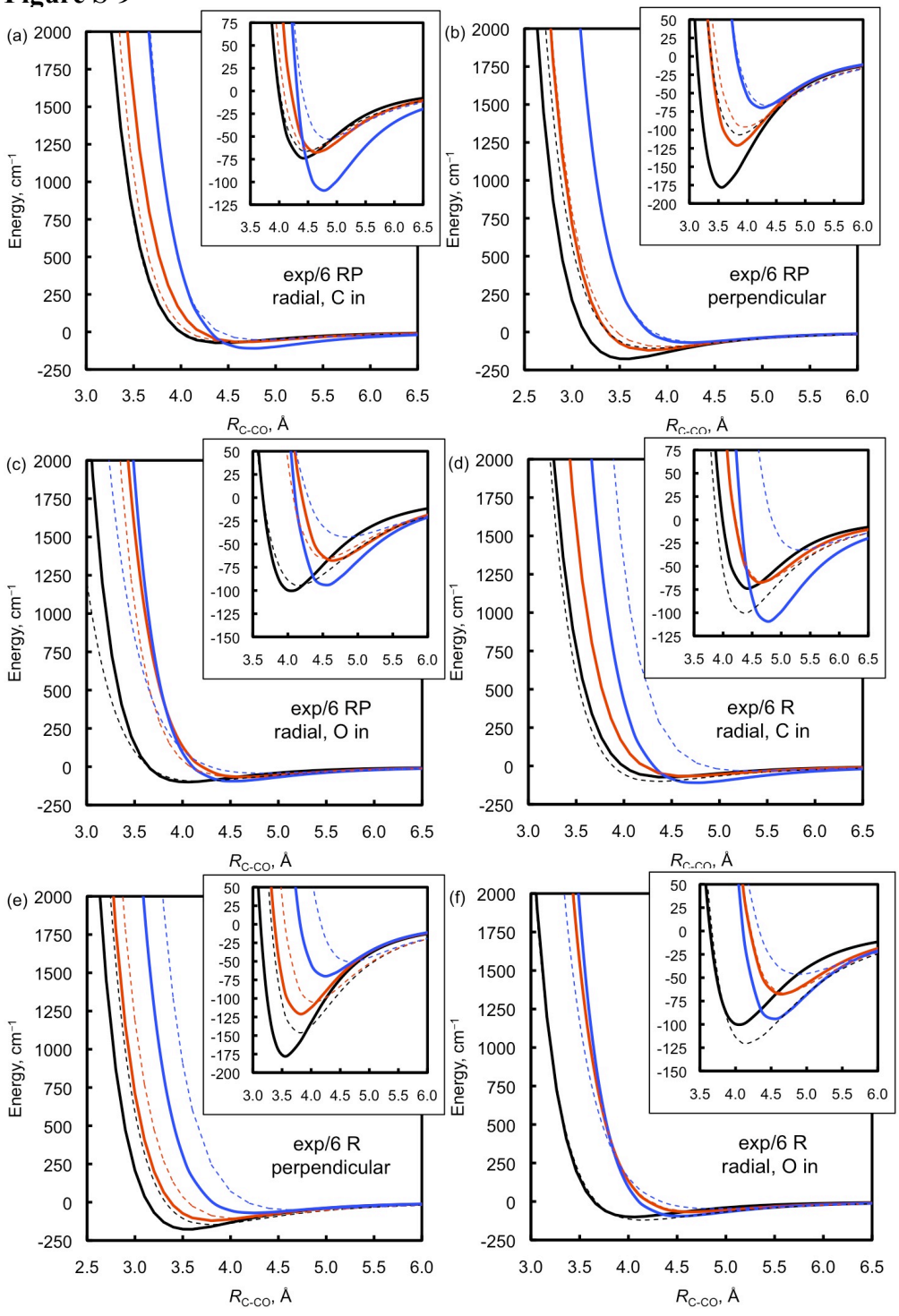

Fig. S-9 Comparison of the QCISD(T)/CBS CH_4 + CO interaction potential (solid) along nine approaches with the exp/6 method for the (a,b,c) compromise (RP) and (d,e,f) O-in radial-only (R) fits (dashed). The color code for the approaches is the same as in Fig. S-2. CO is aligned in the direction of the approach (radially) with C facing CH_4 in (a,d), perpendicularly in (b,e), and radially with O approaching CH_4 in (c,f).